Electronic Supplementary Information

Reactivity of three-coordinate iron-NHC complexes towards phenylselenol and lithium phenylselenide

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Experimental section

General considerations. All syntheses were carried out using standard Schlenk and glove-box techniques, using an inert atmosphere of nitrogen or argon. Toluene and thf were dried by refluxing over molten potassium, distilled and then stored over activated 4 Å molecular sieves. Acetonitrile was dried over calcium hydride and distilled onto activated 4 Å molecular sieves. Toluene-d_8 was distilled off molten potassium, and was then stored over activated 4 Å molecular sieves. X-ray diffraction data for complexes **6** and **8** were collected on an Oxford Instruments XCalibur2 diffractometer, using MoKα radiation. Data for **7** were collected on a Bruker APEX-II diffractometer, using CuKα radiation. CrysAlisPro software was used for structure refinement and data reduction. UV/Vis spectra were measured using a Camspec M501 Single Beam Scanning UV/Visible Spectrophotometer. Magnetic moments of complexes **6-8** were recorded using the Evans method, using either deuterated toluene or acetonitrile as the solvent, and a protio-toluene capillary insert. $[(IPr)Fe\{N(SiMe_3)_2\}_2]_2$ (1), $[(I^tBu)Fe\{N(SiMe_3)_2\}_2]_2$ (3) and PhSeH were synthesized according to literature procedures. Appropriate citations are provided in the main manuscript. NMR spectra were acquired on a Bruker 400 MHz spectrometer at 298 K. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University, U.K.

Synthesis of [(IPr)Fe(N″)(SePh)] (6). A solution of $[Fe(N'')_2]$ (0.17 g, 0.43 mmol) and IPr (0.17g, 0.43 mmol) in toluene (10 mL) and stirred for a period of 30 minutess at room temperature. The solution was then cooled to –78°C and a suspension of LiSePh (0.075 g, 0.46 mmol) in toluene (10 mL) was added, and the reaction mixture was warmed to room temperature and stirred for three hours. The colour of the solution changed to light brown, and darkened after stirring for 12 hours. The filtered solution was concentrated *in vacuo* and stored at –30°C overnight, yielding a crop of colourless crystals (0.050 g, 15% based on Fe; the low isolated yield is due to the very high solubility of the material in toluene). Calculated elemental analysis C 61.56% H 7.82% N 5.52%; found C 61.53%, H 8.01%, N 5.35%. ^{1}H NMR (toluene-d_8): 51.97, 9.69 with shoulder, 6.63, 4.43 with shoulder, 2.91, 1.70, 1.19, 0.29, 0.12, –16.25, –19.12, –42.12. UV/vis: λ_{max} = 430 nm. Evans method: μ_{eff} = 5.2(6) μ_B (0.038 g/mL).

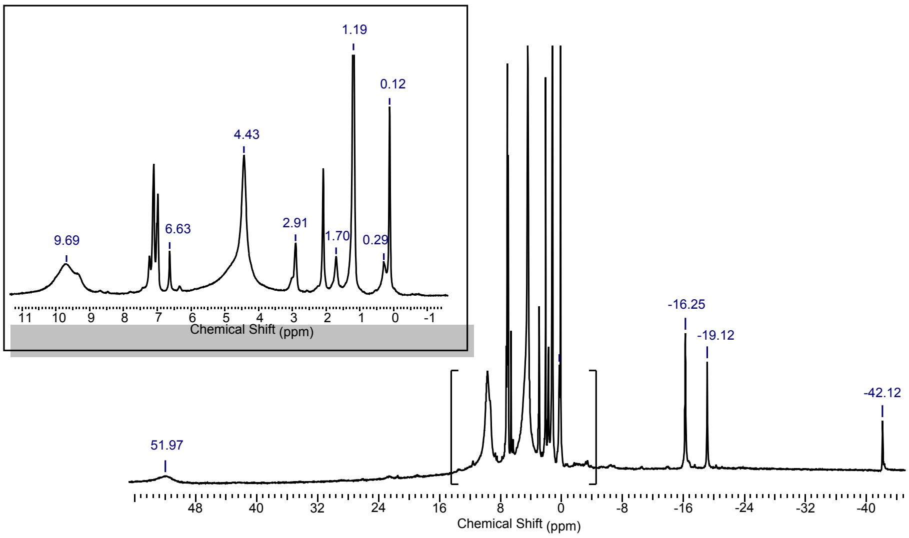

Fig. S1. ^{1}H NMR spectrum of [(IPr)Fe(N″)(SePh)] (**6**) in toluene-d_8.

Synthesis of [I^{t}Bu(H)][(aI^{t}Bu)Fe(SePh)$_3$]·thf, [I^{t}Bu(H)][7]·thf. A solution of [Fe(N″)$_2$] (0.23g, 0.60 mmol) and I^{t}Bu (0.11 g, 0.6 mmol) in toluene (20 mL) was stirred for 30 minutes at room temperature. The solution was cooled to –78°C and PhSeH (0.05 mL, 0.46 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for three hours, during which time the colour of the solution changed from dark green to light brown, with a yellow/brown precipitate. The toluene was removed *in vacuo* and thf (20 mL) was added, yielding a dark brown solution and a light-coloured insoluble solid, which dissolved upon refluxing the solution for *ca.* 1 minute. The thf solution was reduced in volume and stored at –30°C for 10 days, yielding [I^{t}Bu(H)][7]·thf as a crop of yellow crystals (0.045 g, 20% based on PhSeH). Calculated elemental analysis C 54.25% H 6.37% N 6.33%; found C 54.20%, H 6.32%, N 6.29%. ^{1}H NMR (acetonitrile-d_3): 33.99 (imidazolylidene H), 17.86 and 16.83 (*ortho*/*meta* H), 11.60 (imidazolylidene ^{t}Bu), 7.46 (imidazolium H) 6.70 (imidazolium), 4.26 (imidazolylidene ^{t}Bu), 3.70 (thf), 1.83 (thf), 1.58 (imidazolium ^{t}Bu), –2.39 (imidazolylidene H), –9.17 (*para*-H), –11.23 (*para*-H), –16.29 and –17.25 (*meta*/*ortho* H). UV/vis: $\lambda_{\max}$ = 420 nm. Evans method: μ_{eff} = 5.9(6) μ_B (0.025 g/mL).

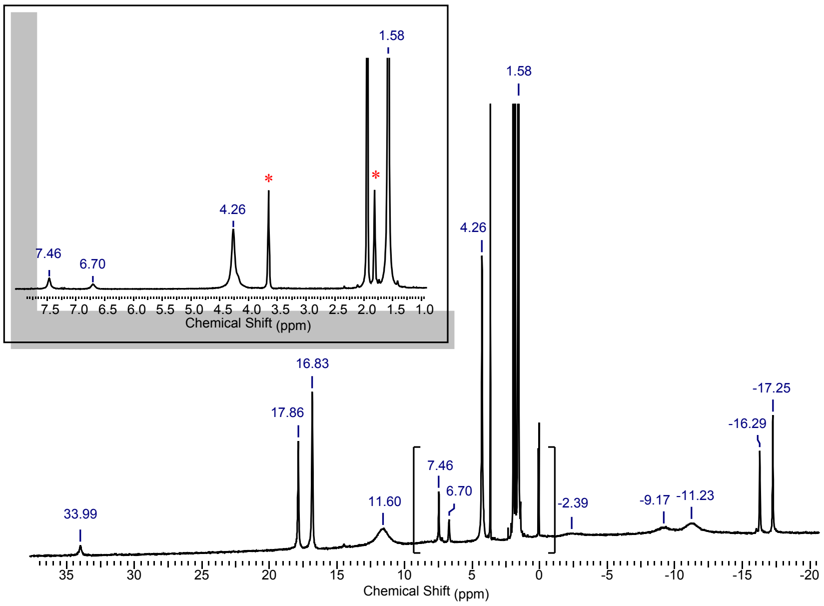

Fig. S2. ^{1}H NMR spectrum of [I^{t}Bu(H)][(aI^{t}Bu)Fe(SePh)$_3$], [I^{t}Bu(H)][7], in acetonitrile-d_3.

Synthesis of [I^{t}Bu(H)]$_2$[Fe(SePh)$_4$]·2(MeCN), [I^{t}Bu(H)]$_2$[8]·2(MeCN). A solution of [Fe(N″)$_2$] (0.19 g, 0.50 mmol) and I^{t}Bu (0.09 g, 0.50 mmol) in toluene (20 mL) was stirred for 30 mins at room temperature. The solution was then cooled to –78°C and PhSeH (0.11 mL, 1.00 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for an additional three hours, during which time the colour of the solution changed from dark green to light brown, and a dark sticky precipitate formed. The toluene was removed *in vacuo* and thf (20 mL) was added, yielding a dark brown solution and an insoluble green solid. The mixture was filtered and the solid was washed with thf (10 mL), and then dried *in vacuo*. The solid was then extracted into acetonitrile (15 mL) and filtered; the volume of the solution was reduced until solid material began to be deposited on the walls of the Schlenk tube. The solid was redissolved and the solution stored at –30°C overnight, which resulted in the formation of bright green crystals. A second crop was obtained by reducing the volume and recrystallizing at –30°C (total yield = 0.057g, 7% based on PhSeH – the low isolated yield is due to the very high solubility of the material in acetonitrile). Calculated elemental analysis C 52.99%, H 5.99%, N 5.37%; found C 52.84%, H 5.90%, N 5.47%. ^{1}H NMR (acetonitrile-d_3): 17.85 (*ortho*/*meta* H), 8.31 (2H, imidazolium H), 7.44 (4H, imidazolium H), 1.56 (36H, imidazolium ^{t}Bu), –9.16 (*para* H), –16.29 (*ortho*/*meta* H). UV/vis: $\lambda_{\max}$ = 408 nm. Evans method: μ_{eff} = 5.4(2) μ_B (0.027 g/mL).

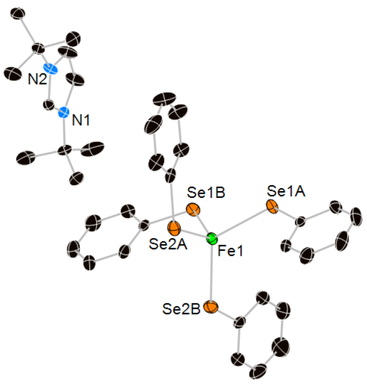

Fig. S3. Structure of [I^{t}Bu(H)]$_2$[Fe(SePh)$_4$], showing only one [I^{t}Bu(H)]$^+$ cation. Thermal ellipsoids set at 50% probability. Hydrogen atoms are not shown.

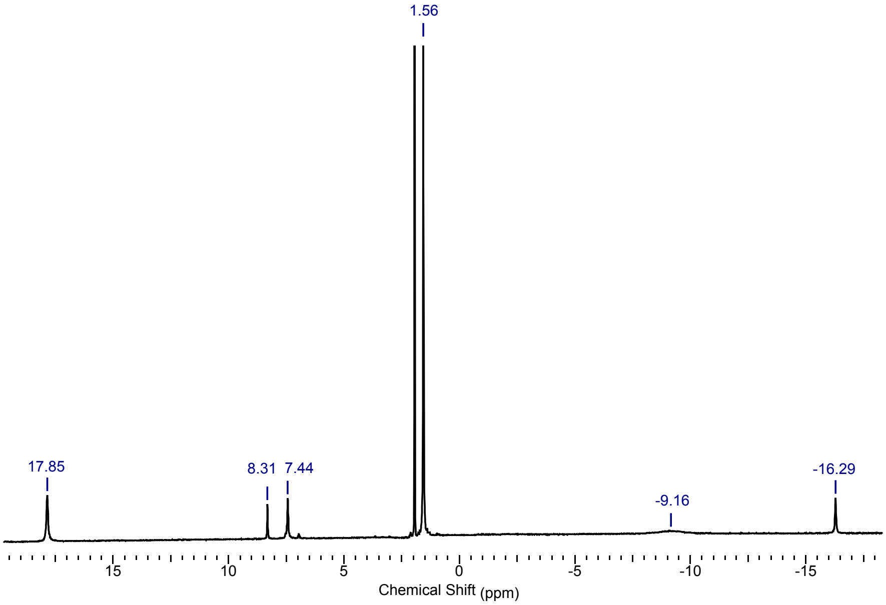

Fig. S4. ^{1}H NMR spectrum of [I^{t}Bu(H)]$_2$[Fe(SePh)$_4$], [I^{t}Bu(H)]$_2$[**8**], in CD$_3$CN.

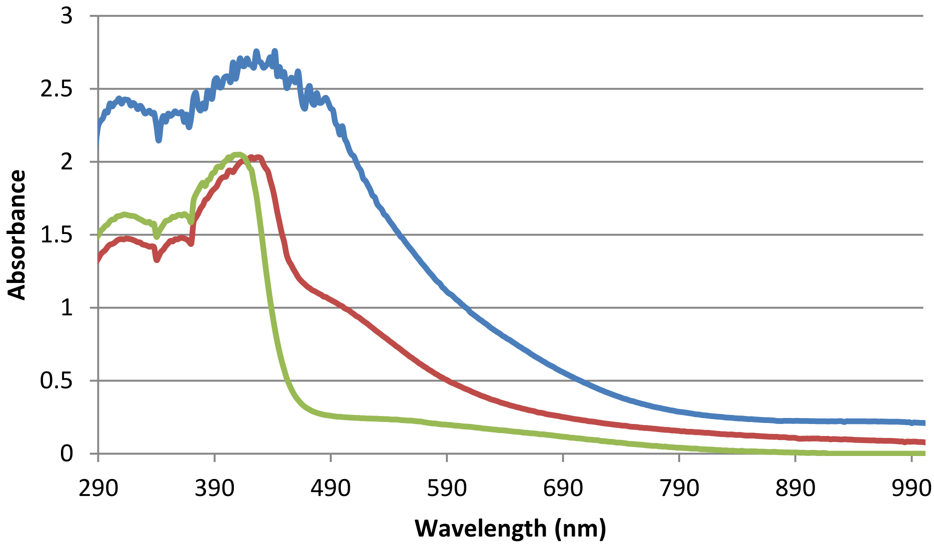

Fig. S5. UV/vis spectra of **6** (blue, toluene), [I^{t}Bu(H)][**7**] (red, MeCN) and [I^{t}Bu(H)]$_2$[**8**] (green, MeCN).

Table S1. Crystal data and structure refinement for **6**, [I^{t}Bu(H)][**7**]·thf and [I^{t}Bu(H)]$_2$[**8**]·2(MeCN).

	6	**[I^{t}Bu(H)][7]·thf**	**[I^{t}Bu(H)]$_2$[8]·2(MeCN)**
CCDC ref. code	971588	971589	971590
Empirical formula	$C_{39}H_{59}N_3Si_2FeSe$	$C_{44}H_{64}N_4OFeSe_3$	$C_{50}H_{68}N_6FeSe_4$
Formula weight	760.88	957.72	1124.79
T/K	150.04(13)	100.0	150.03(10)
Crystal system	monoclinic	monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$
a/Å	12.5662(4)	20.4281(4)	18.1328(7)
b/Å	18.9572(5)	9.40903(17)	11.4406(3)
c/Å	17.9664(8)	24.0280(4)	25.8000(9)
α/°	90	90	90
β/°	107.200(4)	103.3807(16)	98.655(4)
γ/°	90	90	90
V/Å^3	4088.5(3)	4493.02(13)	5291.3(3)
Z	4	4	4
Density (calculated)/Mg m^{-3}	1.236	1.416	1.412
Crystal size/mm^3	0.17 × 0.07 × 0.05	0.32 × 0.26 × 0.15	0.30 × 0.30 × 0.20
2θ range for data collection/°	6.842-52.744	14.778-133.198	7.124 to 52.744°
Reflections collected	13520	20942	10803
Independent reflections	8272 [R(int) = 0.0370]	7709 [R(int) = 0.0824]	5419 [R(int) = 0.0356]
Completeness/%	98.9	97.2	99.7
Data/restraints/parameters	8272/0/429	7709/0/490	5419/0/283
Goodness-of-fit on F^2	1.041	1.043	1.032
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0539$, $wR_2 = 0.0912$	$R_1 = 0.0561$, $wR_2 = 0.1415$	$R_1 = 0.0420$, $wR_2 = 0.0824$
R indices (all data)	$R_1 = 0.0870$, $wR_2 = 0.1047$	$R_1 = 0.0675$, $wR_2 = 0.1530$	$R_1 = 0.0598$, $wR_2 = 0.0902$
Largest diff. peak, hole/e.Å^{-3}	0.60, –0.78	0.97, –1.03	0.88, –0.74